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Vienna, Austria, 26 - 30 March 1979

ETHANOL - AN ALTERNATIVE TO ITS USE AS A FUEL*

by

P. J. Johnston**

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ETHANOL - AN ALTERNATIVE TO ITS USE AS A FUEL*

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The presentation will cover a description of ethanol as a business, its uses as a solvent and intermediate in today's marketplace. In the past, over 70 organic chemicals were derived from ethanol, one of the original building blocks of the chemical process industry in the United States.

Ethanol's potential in this area will be reviewed with brief descriptions of various processes, conditions of temperature and pressure, catalysts, and nature of the equipment used.

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The addition of ethanol to gasoline to supplement petroleum supplies, enhance engine performance, or dispose of agricultural surpluses is not a new idea. The concept is almost as old as the internal combustion engine itself. Before and during World War II, in more than fifteen countries, alcohol was and still is the means to extend a nation's limited petroleum resources. The alcohol fuel has been derived from molasses, wine, grain, potatoes, wood liquors from papermaking and even from coal.

In the United States, during the depression of the 1930's, several companies were organized to produce alcohol to assist farmers in converting their grain harvests into usable fuel. Despite a corn price of $0.35 per bushel and unlimited cheap natural gas, these plants went bankrupt in two years. At the present time, we in the United States are in the middle of a debate over the addition of ten percent alcohol to gasoline motor fuel. It is proposed that use of this gasohol will reduce the dependency of the United States on imported oil and yield a better return to the American farmer for his labors. Both are noble goals, to be sure, but since the United States consumes over 300 million tons of gasoline each year, the volume of ethanol that would be required to replace 10 per cent of it is equivalent to two and one half times the world's entire annual consumption from all sources on a 95 per cent basis.

Brazil's national alcohol program has been widely heralded. Brazil is a major sugar producer, has arable land available to expand cane and cassava production and an ample supply of labor for agriculture, and, apparently, a balance of payments problem of manageable size. The government has decreed a timetable not only for the use of gasohol in automobiles, but also for the eventual conversion to an all-alcohol fueled car. Little resistance to any part of this program has been noted by the world press.

Yet, something is wrong. In the September 8, 1978 issue of European Chemical News, the commercial director for Petrobras, Brazil's national oil company, stated that the high cost of alcohol, at $.91 per liter, compared to the price for gasoline derived from imported oil at $.47 per liter, forced a reconsideration of the program. Later, in the January 1, 1979 issue of Chemical Engineering, Brazil's Minister of Energy declared that Brazil should export its alcohol because prices in the international ethanol market were twice those of gasoline. The President of Brazil's Council for Scientific Development has stated that alcohol is more important as an industrial raw material than as a combustible. Obviously, the impact of Brazil's ethanol production suddenly redirected to the international market would make that market of only 310,000 tons per year look unattractive as well.

Agricultural production is usually cyclical in nature. The recent meteoric rise in world petroleum prices occurred just as prices for sugar and molasses peaked, then plummeted. The furor over gasohol in the United States is probably due to three bin-bursting grain harvests, in as many years, since the shortages felt by the world in 1972, 1973 and 1974. The U. S. government most likely will support the construction of several fermentation alcohol plants, but when the cycle turns and grain prices rise again, our forecast is that production from those plants will be directed to the industrial market where better pricing can be found -- just as the Brazilians are doing now.

This is not to say that gasohol is the wrong idea for all countries. In fact, because petroleum resources are limited, we anticipate that by the last decade of this century, fuels from renewable resources will be very important to many nations' economies. Those nations endowed with good climate, a wealth of sunlight, arable land, and adequate labor may find that an alcohol fuels program suits them perfectly. They may be able to justify the government subsidies which will be necessary to support construction of the distilleries, inventory the crop surpluses, accumulate the residues for use as fuel, and finally arrange for the distribution of the alcohol.

We all know that alcohol is a very fine fuel. We also realize that it's consumption as a fuel will require large expenditures of tax money and in the end w'll be subject to the vagaries of market demand. Who, in the near future, will put sugar or grain into gasoline if they are able to dispose of their total production in the world market at much higher prices? Who will be willing to continue to support the tax programs necessary for an alcohol program when the market has turned the other way? Is there an alternative that permits the use of renewable resources until such time as the price of petroleum completely justifies a fuel program?

Actually, there are three alternatives to consider: Ethanol can be used as a solvent, reacted with other chemicals, or resume its role as a building block for the chemical industry.

THE UNITED STATES ETHANOL MARKET

In 1978, the United States consumed about 705,000 tons of ethanol in the industrial market and 200,000 tons in the beverage market. About ten percent of current demand in the industrial market is supplied by imports, primarily from Argentina, Canada and the United Kingdom. This rather high percentage is due to the very low duty the United States applies to imported ethanol for industrial use -- currently only 2.5 per cent of the selling price -- and to the economic environment in other countries that has made the large United States market look so attractive. This volume represents almost one fourth of the annual international trade in industrial ethanol and both Shell Chemical and B.P. Chemical have announced plans to construct a total of 475,000 tons of synthetic ethanol capacity by 1983 in Saudi Arabia and Scotland with much of the production slated for export to the United States and elsewhere. By the mid 1980's, then, we expect that the United States probably will be abundantly supplied with ethanol.

Beginning in the mid-1930's, using the same cheap natural gas that was available to the Midwest grain alcohol plants, Union Carbide built a business based on ethyl alcohol, but made from ethylene. At one time, over 70 organic chemicals derived from ethanol were offered for sale by the company. Its customers in turn probably doubled that number in development of useful products based on ethanol. Today, as a result of competing technologies, ethanol is no longer the foundation of the chemical process industry in the United States, but it is a fair sized business. Union Carbide is still one of the largest consumers of ethanol in the world, but over 70 per cent of its production in 1978 was sold to more than 600 customers in 46 states. Shipments to these customers are made in rail tank cars, tank trucks, drums, pails, and cans. Six terminals located in major markets are supplied by barge, ship or rail tank car from a single plant at Texas City, Texas.

Slightly more than half the alcohol sold in the U.S. is used as a solvent. Nitrocellulose coatings, printing inks, shellacs and varnishes, and light and heavy liquid detergents contain ethanol, demonstrating the solvent power and versatility of the product. The cosmetic and pharmaceutical markets rely on ethanol's purity, miscibility with water and evaporation rate to produce perfumes, toiletries, mouthwashes, antiseptics, vitamins and antibiotics. The characteristically high value of these products is enhanced by the availability of non-taxable ethanol, rendered unfit for beverage use by suitable denaturation. The food industry uses ethanol both as a solvent and as an intermediate in flavorings, extracts, colorings and vinegar. Vinegar, a very important ethanol derivative, demonstrates its own versatility by serving as a preservative, flavoring and acidulant.

Automobile coatings, brake fluids, house paints, hydraulic fluids and lubricants, herbicides, pesticides and explosives consume ethanol at some point in their manufacture. The investment casting process for prosthetics, machine parts, turbine blades and golf clubs is based largely on ethyl silicate hydrolyzed by further reaction with ethanol. Before 1970, automobile tires, seat covers and the interlayer in laminated safety glass were major outlets for acetaldehyde generated from alcohol. Still earlier, ethanol was widely used as an antifreeze in automobile radiators.

Today, many of these products are the beneficiaries of newer technologies that replaced acetaldehyde and ethanol. Ethanol is still reacted with ethylene oxide to form glycol ethers, with acrylic and acetic acids to form esters, with ammonia to form amines, and with acetylene to form a vinyl ether useful in pressure sensitive adhesives and other coatings. By the end of this century, we may have come full circle in the United States, with ethanol regaining the preeminent position occupied by ethylene today. It is a good bet that some of that alcohol will be produced by fermentation from renewable resources. Those countries without an entrenched chemical industry with established ethylene plants might find it very worthwhile to consider establishing a chemical business based on ethanol that would add value to their agricultural products, provide employment for people with a variety of skills, and promote the general welfare by increasing the supply of consumer products.

THE BUILDING BLOCK

Ethanol's use as a chemical would seem to be a permanent one in which a nation might invest because it requires more modest production volumes, lower capital investments and therefore lower government subsidies.

Objections to such a plan are probably based on the fear of practicing obsolete technology, or the feeling that the market for the product is not as developed as that for petroleum or gasoline. Ethanol's versatility, flexibility and acceptability, coupled with marketing expertise available through conferences such as this, or by consultation, should alleviate anyone's concern that the market may not be there.

On the technical side, I prefer to view the technology as assured or safe, rather than as obsolete. Union Carbide closed its 80,000-ton-per-year acetaldehyde-from-ethanol plant in March, 1978. It had operated for almost 40 years and had continued in service past 1975 because it provided the only source of hydrogen for several important products. Publicker Chemical and Texas Eastman are two U.S. companies believed to still be producing acetaldehyde and acetic acid from alcohol. Union Carbide has plants in India and Brazil at which ethanol continues to be an important building block.

Earlier, I mentioned that over 70 products could be derived directly from ethanol. To cover the production of all these would require too much time, but a brief exploration of the technology for several of the most important chemicals may prove interesting. The production processes for ethanol from renewable resources will be left to others more expert in that area.

ETHYLENE

The economical production of ethylene by dehydration of ethanol would assure a bright future for a chemical industry based on renewable raw materials. The simplicity of the reaction eliminates the burden of finding outlets for any number of byproducts, and the largest part of the production cost is the ethanol feedstock, whereas in using naphtha, 55-60 per cent of the cost is capital related. A dehydration unit should be part of the complex which will consume the ethylene since the transport of ethylene requires liquefaction which raises the cost to the downstream users by as much as $100 to $150 per ton.

Production of ethylene from ethanol is carried out at 300°C, and that temperature is critical: if it runs too high, an excess of aldehydes results; if too low, ether production dominates. Ethanol is usually dehydrated in several fixed beds over a variety of catalysts, including alumina, silica aluminas, activated alumina, hafnium and zirconium oxides, and phosphoric acid on coke. These fixed-bed catalysts are regenerated every three weeks or so with steam and air to remove carbon deposits. This process requires about 1.7 to 2.0 tons of alcohol per ton of ethylene -- an 85-90% yield and produces ethylene with a purity of 95 per cent or better. The ethanol feedstock need not be anhydrous; 94.5 percent or 189 proof is sufficient.

A 60,000-ton-per-year unit would require about 90 employees for operation and maintainance, depending on whether it used a fixed bed or fluidized bed process would be expected to cost $4 to $8 million within the battery limits.

C. E. Lummus recently published (Hydrocarbon Processing, Feb. 1978) a description of a fluidized bed process for ethanol to ethylene which appears to offer lower capitol costs, better temperature control, and concurrent catalyst regeneration which would permit more continuous operation. Higher purity ethylene is also obtained by this route.

ACETALDEHYDE

In peak periods, over 460,000 tons of acetaldehyde were produced in the United States per year. It was the most important of the ethyl derivatives until the early 1970's. Acetaldehyde may be produced from 190-193 proof ethanol either by dehydrogenation or oxidation. Dehydrogenation is endothermic, but the recovery of the hydrogen allows f[illegible] production of butanol, ethylhexanol and other reduction products. Dehydrogenation is carried out in the vapor phase over a chromium-activated, copper catalyst at 320°C. The unreacted ethanol is recycled with a conversion rate of 50 per cent per pass. One ton of acetaldehyde (99.7 per cent purity) is produced from 1.2 tons of ethanol, or a 90 per cent yield. Other catalysts have been used with varying degrees of success. A 40,000 ton unit would cost $10 to $15 million and would require fewer than 20 employees for its operation.

The oxidation route may be accomplished in either the vapor or liquid phase. In the vapor phase at 475°C, air and a copper or silver catalyst gives 80 per cent conversion per pass. The reaction in the liquid phase, in the absence of free air but at atmospheric pressure and 80°C, is catlyzed by chloroplatinic acid and yields acetaldehyde at 95 per cent or better.

HYDROGEN

Before deciding whether to produce acetaldehyde by oxidation or dehydrogenation, one should remember that the availability of hydrogen increases the flexibility and versatility of the chemical plant. The production of butanol or ethylhexanol requires hydrogen, but the conversion of benzene to cyclohexane, the reduction of fusel oil byproducts, or the use of hydrogen as a fuel directly or in fuel cells should not be overlooked. Recovered hydrogen on a water free basis has a purity of 99 per cent the contaminants being methane, ethane, nitrogen, and carbon monoxide and dioxide. Usually the product is used as is with a 2 per cent water content, which causes few if any problems to downstream consumers.

Storage is necessary, and Union Carbide used several miles of an abandoned natural gas transmission line for that purpose with good results and no special equipment other than a compressor to raise pressure to 100 atmospheres.

n-BUTANOL AND BUTYRALDEHYDE

Butanol is an important intermediate for the production of coatings and adhesives, hydraulic fluids and lubricants, degreasers and plasticizers. For almost 40 years, Union Carbide operated a 25,000-ton butanol-from-acetaldehyde plant at Texas City, Texas, A new, 30,000-ton plant today would cost $15 to $20 million direct battery limits investment, and require 20 to 25 operators and supervisors.

The process which produces one ton of butanol from 1.73 tons of ethanol takes place in three steps from acetaldehyde. In the first, acetaldehyde is mixed with dilute (25 per cent) caustic in a stirred-tank reactor with sufficient cooling to absorb the exotherm. After neutralization, the aldol and unreacted acetaldehyde are contacted with boiling sulphuric acid to form crotonaldehyde. The crotonaldehyde is removed from the converter as quickly as it is formed to avoid decomposition. It is then refined and the unreacted acetaldehyde and acetaldol are recycled. The crotonaldehyde (99 per cent purity) is next hydrogenated in the vapor phase and the resulting n-butanol is recovered by azeotropic distillation, decantation and batch dehydration. The entire process has an efficiency of 97 per cent to n-butanol and produces butyraldehyde as a byproduct.

ETHYLHEXANOL

Surface-active agents, plasticizers, oil additives and paint dryers are but a few of the products derived from ethylhexanol. Today, this chemical is produced by the condensation of butyraldehyde. In this reaction, 1.18 tons of butyraldehyde (water-saturated to retard condensation during storage) is treated with 1.5 per cent caustic in a stirred tank reactor at 105°C. Higher temperatures increase undesirable residue production. From a decanter, the lower water layer containing caustic is recycled, and the upper layer of ethylpropyl acrolein is fed directly to a liquid-phase hydrogenator at a pressure of 25 atmospheres over a nickel, cobalt or copper and chromium catalyst. The crude product is then refined in a two-column batch distillation unit. A 40,000 ton unit would require 12 to 15 operators and would cost about $15 million battery limits.

BUTADIENE

This valuable chemical intermediate for automobile tires, plastics, adhesives, coatings and textiles is generally produced today by naphtha cracking or the dehydrogenation of butane and butenes. During World War II, however, almost two-thirds of U. S. production was from ethanol via the Ostromisslenski process. A three-to-one mixture of ethanol and acetaldehyde is treated with dilute caustic at subambient temperatures. The resulting aldol is then cracked over a fixed-bed catalyst of tantalum oxide and silica gel at 325-350°C. One ton of butadiene of 98 per cent purity is produced from 2.76 tons of ethanol (including that consumed in acetaldehyde). A 42,000 ton unit would require 35 to 40 people to operate with a battery limits investment of about $50 million.

ACETIC ACID AND ACETIC ANHYDRIDE

These two products are widely used in the production of dyes, monomers, pharmaceuti ls, flavorings and tex le finishes. Th may be produced together in the dual-acid process in which acetaldehyde is air-oxidized in a stirred reactor over a copper and manganese or copper and chromium catalyst. The reaction takes place in the liquid phase at 55-66°C and at a pressure of 5 atmospheres. Production of one ton of acetic anhydride requires 1.42 tons of acetaldehyde and 2.27 tons of compressed air. For each ton of anhydride, the yield of acetic acid is .625 tons and the yield of 98 per cent pure nitrogen is 1.6 tons at a pressure of seven atmospheres. Union Caribde operated a 60,000-ton unit at Texas City, Texas until 1970, using two operators per shift.

Oxidation with pure oxygen at lower pressure and at 80-85°C is possible and vapor-phase reaction over a silver catalyst at 540°C has also been reported.

SUMMARY

A number of these processes could very easily be consolidated in one complex or, in a few cases, produced in campaigns in the same equipment. Consolidation would reduce the number of operators and maintenance people required and would offer the benefits of economy of scale in non-battery limits investment for power plants, storage tanks, a distribution terminal and pollution abatement. Not only is it possible to consider burning bagasse or other agricultural waste to provide part of the facility's fuel requirements, but residues from a number of processes would be a reliable fuel supply also.

The most important factor in the cost of these products is the price of the ethanol. For the next few years, production of the ethanol will require subsidies to assure that facilities are built and markets are developed. Total capital costs will depend on the size of the facility but it is recommended that the units be designed to serve intranational demand rather than export markets. The reality is that chemical products from olefins will continue to be more economical than ethanol derivatives, at least for the near future.

What has been proposed here is an alternative to burning ethanol as fuel, although the fuel use may in the long run be a logical choice for several countries or areas. It is my belief, however, that just as the chemical use of petroleum is so much smaller than the demand to power automobiles, the chemical use of our renewable resources will require far less in the way of investment, subsidies, and distribution and would be a project of more manageable size for those countries concerned about the demands on its infrastructure.

It is an alternative with a future because no matter what development renders the internal combustion engine obsolete, the chemicals that can be derived from ethanol will probably always be important to our economies. But since it is an alternative, it implies choice, and that choice can only be made by each nation acting in its own best interest.

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